CdS/HgS/CdS Quantum Dot Quantum Wells: A Tight-binding Study

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Abstract

We study the electronic properties of spherical quantum dot quantum well nanocrystals within a symmetry-based tight-binding model. In particular, the influence of a concentric monolayer of HgS embedded in a spherical CdS nanocrystal of diameter 52.7 Å is analyzed as a function of its distance from the center. The electron and hole states around the energy gap show a strong localization in the HgS well and the neighboring inner (core) interface region. Important effects on the optical properties such as the absorption gap and the fine structure of the exciton spectrum are also reported.

I. INTRODUCTION

The interest in semiconductor nanocrystals (NC's) or quantum dots (QD's) was first awakened by the size dependence of their electronic properties which could allow, in principle, the manufacture of sensor, lasers, etc. with specific features. One step further was the inclusion of a layer of a different compound HgS in a CdS NC, for example, which produces additional drastic changes in the optical properties in such quantum dot quantum well (QDQW) NC's [1, 2]. In fact, one of the primary objectives of this manipulation was to avoid the, undesirable, surface effects in the electronic states near the band gap [3]. In addition to the CdS/HgS/CdS case, systems based on ZnS/CdS [4] have been studied.

On the theoretical side, a single band effective mass approximation (EMA) model was first proposed [1] followed by a multiband EMA analysis [5]. An atomistic theory was needed, however, to adequately describe a QDQW where the well could be as thin as one monolayer. Recently, a tight-binding (TB) model has been proposed for CdS/HgS/CdS and ZnS/CdS/ZnS QDQW's [4, 6]. This model assumed, however, some simplifications: Instead of zincblende, fcc structured NC's were studied and, also, the spin-orbit coupling was neglected. Here we propose a symmetry-based TB theory which has been previously used to account for the optical properties of CdSe [7] and CdTe [8] NC's. Also, we take the zincblende crystalline structure of the actual dots. We investigate the influence of the HgS layer on the electronic and optical properties. In particular, it is found that the charge distribution, gap and the fine structure of the exciton spectrum are strongly dependent on the distance of the monolayer from the NC center. Finally, we compare our results with the available experimental data.

II. THEORY

The calculation of the one-particle TB Hamiltonian has been previously described in detail [8]. It is based on a semi-empirical TB model for semiconductors [9] which accounts for the bulk properties. The interatomic hopping matrix elements are restricted to the nearest neighbors. The CdS TB parameters used here are an adequate modification of those proposed earlier [10] to take now into account the finite spin-orbit coupling. The HgS parameters have been obtained from the CdS ones and account for the small bulk gap, 0.2

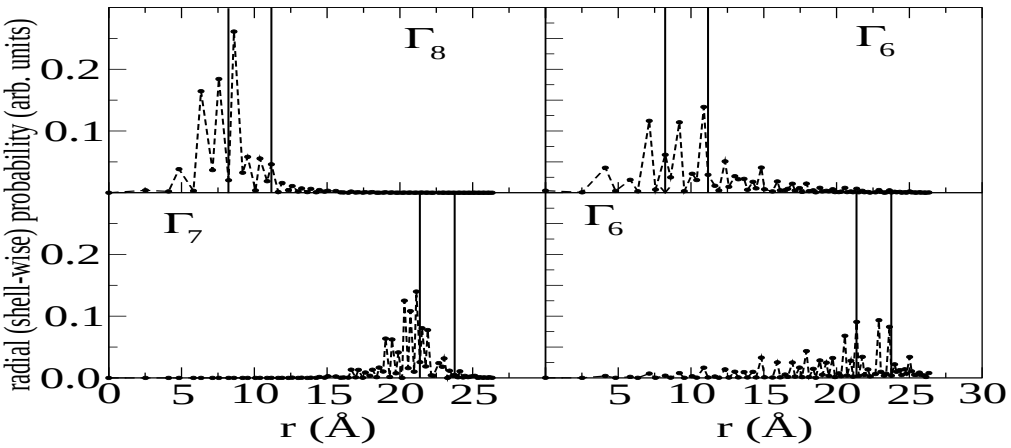

Figure 1: Radial (shell-wise) probability of the HOMO (left) and LUMO (right). The radius of the core, size of the well and clad are 8.2/3/15.1 Å (top) and 21.4/2.4/2.5 Å (bottom). Vertical bars indicate the HgS shell. The symmetry is also indicated

eV, and the shift of the HgS valence band of 0.85 eV as in Ref. [11]. We passivate the NC surface by placing a hydrogen s orbital at each empty nearest-neighbor site on the surface (dangling bond). We saturate the bonds so that the surface states are several eV far from the gap edges. The NC's, of roughly spherical shape, are constructed starting from a cation at the origin by successively adding nearest-neighbor atoms through tetrahedral bonding. In this work we study a NC with a fixed number of atoms, 3109, equivalent to a diameter of 52.7 Å. We use hereafter the word "shell" to indicate the collection of atoms which are at the same distance from the center. A chemical monolayer contains several shells and their number depends on the layer radius. We reduce the Hamiltonian to a block diagonal form by writing it in a symmetrized basis corresponding to the double-valued representations Γ_k ($k = 6, 7, 8$) of T_d.

When the Coulomb interaction is introduced the total Hamiltonian is written in a many-body electron-hole basis. The details of the simplifying approximations used to write the direct and exchange terms can be found in Ref. [7, 12]. The absorption spectra are computed following a simplified procedure as in [7]. The dipole matrix elements between different orbitals on the same atoms are taken from [13]. The fine structure of the lowest-energy transitions is studied taking into account all the Hamiltonian terms, with as many valence

$r_{co}/r_w/r_{cl}$ (Å)	Core	Well	Clad	electron radius (Å)
21.4/2.4/2.5	0.47(0.81)	0.35(0.12)	0.15(0.06)	19.9
10.9/3.0/12.4	0.23(0.17)	0.41(0.20)	0.33(0.62)	12.7
8.2/3.0/15.1	0.19(0.09)	0.40(0.16)	0.41(0.75)	11.3

Table I: The probability of presence of electron in the LUMO. The core radius and also the well and clad sizes are given in the first column for each case. In parenthesis we show the probability of presence in the case of a simple CdS QD. The fourth column shows the electron radius, to be compared with its value 15.5 Å in a CdS QD

$r_{co}/r_w/r_{cl}$ (Å)	Core	Well	Clad	hole radius (Å)
21.4/2.4/2.5	0.53(0.85)	0.44(0.11)	0.03(0.04)	20.7
10.9/3.0/12.4	0.37(0.08)	0.55(0.21)	0.07(0.71)	10.5
8.2/3.0/15.1	0.25(0.02)	0.63(0.10)	0.12(0.88)	8.5

Table II: The probability of presence of hole in the HOMO. We use the same notations and conventions as in Table I. The hole radius in a CdS QD is 18.5 Å

and conduction states as necessary to reach numerical convergence.

III. RESULTS

In Fig. 1 we show the radial probability of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for two different situations. When the HgS monolayer is included, both the electron and hole show an enhancement of their presence within the well. From Table I and Table II it can be also seen that the hole is always more localized than the electron. Moreover, the wells of smaller radius are more efficient for trapping the particles. Finally, a careful inspection of Fig. 1 shows an increase of the hole density on the inner part of the interface neighborhood. The states nearest in energy to the HOMO and the LUMO show similar shapes.

In Table III we show the values of the HOMO and LUMO energies and the optical gap obtained from the energy of the first allowed exciton state. The overall trend indicates that the gap decreases as the monolayer radius decreases. The gap of the 52.7 Å wide CdS dot, 2.666 eV, is in good agreement with the value measured by Schoss *et al.* [1], 2.62 eV. The

$D = 52.7$ Å	HOMO (eV)	LUMO (eV)	Gap (eV)
26.3/0.0/0.0	-0.093(8)	2.870(6)	2.664
21.4/2.4/2.5	0.284(7)	2.321(6)	1.936 (1.953)
10.9/3.0/12.4	0.333(8)	2.187(6)	1.696(1.768)
8.2/3.0/15.1	0.303(8)	2.285(6)	1.798(1.851)

Table III: The highest (lowest) occupied (unoccupied) valence (conduction) levels in the second (third) column along with the symmetry in parenthesis. The results correspond to a dot of 52.7 Å of diameter. The same cases as in previous tables are considered. The optical gap is given in the last column. We give also the energy of the next important peak in parenthesis (see also Fig. 2)

structure of the lowest energy optical spectra shows also significant differences between the CdS QD and the CdS/HgS/CdS QDQW. In Fig. 2 the absorption spectra of three different dots are shown. The CdS QD presents the first peak at 2.664 eV with a relative intensity of 0.303. Very close in energy there is a more important peak at 2.666 eV which shows an intensity of 5.753. When a HgS monolayer is included the first transition (exciton ground state) gets relatively weaker as the HgS monolayer radius decreases. When the HgS layer radius is 21.4 Å the intensities of the exciton ground state and the states close in energy are smaller than in the CdS QD. As the radius decreases further, at 7.6 Å, there is only a "dark" exciton ground state separated 53 meV from the "bright" states. The agreement with previous EMA [1, 5] and TB [6] calculations is good for the one-electron description: The energies and charge localization. As for the exciton, a comparison is difficult because we take the full many-body Hamiltonian and, also, the QD sizes studied here are smaller.

IV. CONCLUSION

We have presented a TB model adequate to describe NC heterostructures. We have considered the inclusion of a single QW monolayer of HgS in a spherical CdS NC. The HOMO and LUMO states near the gap edges are localized in the QW layer and its proximity. The effects on the optical properties are also important. In particular, the absorption gap decreases when the layer radius decreases. The absorption spectrum also changes: The relative intensity associated with the "dark" exciton state is a decreasing function of the

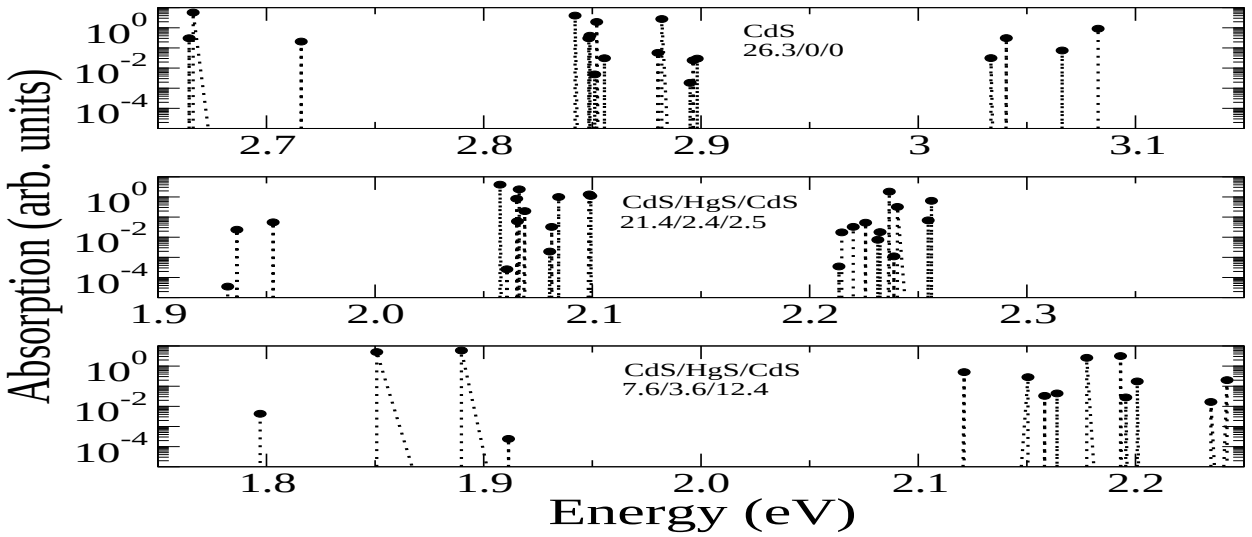

Figure 2: Fine structure of the optical absorption spectrum for three different NC's. We show the same window of energy, 0.5 eV, for each case. The dotted lines help distinguish the different transitions

layer radius.

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